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## PATENT ABSTRACTS OF JAPAN

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## (54) ALKALINE STORAGE BATTERY

## (57)Abstract:

PROBLEM TO BE SOLVED: To suppress the alloy corrosion of a hydrogen storage alloy negative electrode and lengthen the cycle life by adding ytterbium or a ytterbium compound to a nickel hydroxide positive electrode.

SOLUTION: An alkaline storage battery has a positive electrode prepared by adding ytterbium or a ytterbium compound to an active material whose main component is nickel hydroxide. The ytterbium or the ytterbium compound is preferable to exist in the free state from the active material whose main component is nickel hydroxide. The ytterbium or the ytterbium compound is preferable to exist in the positive electrode in the form of an oxide or a hydroxide.

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(54) 【発明の名称】 アルカリ蓄電池

(57) 【要約】

【目的】 ニッケル正極の高温における利用率を高め、水素吸蔵合金負極の合金腐食を抑え、サイクル寿命を高めたニッケル水素化合物蓄電池を提供することを目的とする。

【構成】 ニッケル水酸化物を主成分とする活物質にイッテルビウム又はイッテルビウム化合物を添加してなる正極を備えたアルカリ蓄電池とすることで、上記目的を達成できる。

## 【特許請求の範囲】

【請求項1】 ニッケル水酸化物を主成分とする活物質にイッテルビウム又はイッテルビウム化合物を添加してなる正極を備えたことを特徴とするアルカリ蓄電池。

【請求項2】 前記アルカリ蓄電池において、イッテルビウム又はイッテルビウム化合物が、ニッケル水酸化物を主成分とする活物質と遊離状態で存在している請求項1記載のアルカリ蓄電池。

【請求項3】 前記アルカリ蓄電池において、イッテルビウム又はイッテルビウム化合物が、酸化物あるいは水酸化物の状態で上記正極中に存在している請求項1記載のアルカリ蓄電池。

## 【発明の詳細な説明】

## 【0001】

【発明の属する技術分野】 本発明はニッケル水酸化物および水素吸蔵合金を用いたニッケル水素化物蓄電池に関するものである。

## 【0002】

【従来の技術】 昨今の環境保護の気運に乗り、低公害性のニッケル水素化物蓄電池は、従来のカドミウムを負極に用いるニッケルカドミウム蓄電池に代わる電源としてポータブル機器などに用いられ、研究開発が盛んに行われている。

【0003】 ところで、従来のニッケルカドミウム蓄電池においては、ニッケル正極の高温における利用率を維持するためカドミウムの添加が不可欠であった。低公害性を最大の特徴とするニッケル水素化物蓄電池においては、環境破壊物質であるカドミウムを使用することができないという問題があった。これを解決する手段として、特開平5-290879公報等にみられるように、カルシウム化合物などの各種添加剤を添加する方法が報告されている。しかしながらニッケル水素化物蓄電池においては以下に述べるような問題があり、これら従来添加物では、電池性能改善には不十分であった。一方、水素吸蔵合金は強アルカリ中では合金構成成分である希土類が溶け出し、絶縁性の水酸化物として析出する腐食現象を起こすため、寿命が短くなるという問題があった。

## 【0004】

【発明が解決しようとする課題】 本発明は上記問題点を鑑みてなされたものであり、ニッケル正極の高温における利用率を高め、水素吸蔵合金負極の合金腐食をおさえ、サイクル寿命を高めたニッケル水素化物蓄電池を完成したものである。

## 【0005】

【課題を解決するための手段】 本発明では、ニッケル水素化物蓄電池中のニッケル水酸化物正極にイッテルビウム又はイッテルビウム化合物を添加することで、上記問題点を解決した。

【0006】 イッテルビウムおよびイッテルビウム化合物は強アルカリ中でわずかに溶け、安定な水酸化物とし

て析出する。イッテルビウム水酸化物は酸素発生過電圧を引き上げる効果を持ち、電解液の分解を防止するためニッケル正極の高温における利用率を高める。また溶解したイッテルビウムおよびイッテルビウム化合物は、水素吸蔵合金負極表面に安定な水酸化物として析出する際に被膜を形成し、これが合金成分の腐食を防ぐため、負極の寿命を長くする。

## 【0007】

【発明の実施の形態】 以下に実施例に基づき本発明を説明する。

（実施例1）例えばカドミウムを含まない市販の水酸化ニッケルを準備して、水酸化ニッケル粉末に対し、導電剤として金属Coを重量%で6wt%、CoOを重量%で4wt%となるようにそれぞれ加え、例えばYb<sub>2</sub>O<sub>3</sub>を重量%で2.5%十分に混合した。これに水および増粘剤を加えペースト状にし、例えば、ニッケル繊維基板に充填、乾燥後プレスして本発明ニッケル正極と成し、通常の水素吸蔵合金電極を相手極としアルカリ電解液を用いて、本発明ニッケル水素化物蓄電池を作成した。

【0008】 一方、比較のため上記と同様の組成の水酸化ニッケル粉末に従来添加物として、Ca(OH)<sub>2</sub>を添加したもの、および添加剤を使用しない従来の正極を作成し、同様に通常の水素吸蔵合金電極を相手極としアルカリ電解液を用いて、比較用ニッケル水素化物蓄電池を作成した。この比較用電池はYb<sub>2</sub>O<sub>3</sub>を正極中に含まない以外は本発明ニッケル水素化物蓄電池と全く同じ物である。

【0009】 このようにして作成した本発明ニッケル水素化物蓄電池と比較用ニッケル水素化物蓄電池を用いて、充放電を行った。その結果を図1に、またこれらの電池の酸素発生過電圧を表1それぞれ示す。

## 【0010】

【表1】

電池種類	酸素過電圧
本発明 (Yb <sub>2</sub> O <sub>3</sub> )	60mV
従来例 (Ca(OH) <sub>2</sub> )	53mV
従来例 無添加	51mV

【0011】 図1中で放電利用率は正極合金中のNi(OH)<sub>2</sub>の理論容量を1グラム当たり290mAhとしたときの実際の放電容量を理論容量で割ったものに100をかけたものである。図1から明かなとおり、本発明ニッケル水素化物蓄電池は高温においても十分な容量を維持していることがわかる。また、表1から明らかな通り本発明の酸素過電圧は従来例に比べて高く、これにより電解液の分解が抑えられ、電池の容量低下を防止できる。

【0012】 更に、サイクル試験を行った後の電池を解

体し、負極から水素吸蔵合金を取り出して、X線回折を行った結果を図2に示す。図2よりあきらかなように本発明である $Yb_2O_3$ を添加したものは、2シータ29度付近の希土類水酸化物のピークが小さく、合金腐食が抑えられていることが分かる。

【0013】（実施例2）例えば実施例1と同様に水酸化ニッケル粉末に対し、導電剤として金属Coを重量%で6wt%、CoOを重量%で4wt%となるようにそれぞれ加え、種々の量の $Yb_2O_3$ を加え、さらに水および増粘剤を加えペースト状にし、例えば、ニッケル繊維基板に充填、乾燥後プレスして水酸化ニッケル正極を作成した。 $Yb_2O_3$ の添加量は表2にまとめて示す。

【0014】

【表2】

電池番号	$Yb_2O_3$ 添加量%
1	0.1
2	0.5
3	1.0
4	2.5
5	5.0
6	10.0
7	0

【0015】この水酸化ニッケル正極に通常の水素吸蔵合金電極を相手極とし、アルカリ電解液を用いて、ニッケル水素化物蓄電池を作製した。この電池を用いて、充放電を行った。その結果を図3に示す。図3から明かなとおり、 $Yb_2O_3$ を添加することにより高温性能が改善されていることが分かる。但し、5%以上の添加では常温での利用率が悪くなり、0.5%以下の添加では高温での効果が弱くなるため、重量%で0.5から5.0%の添加が望ましい。

【0016】

【発明の効果】上記のように、本発明のニッケル水素化物蓄電池では、水酸化ニッケル正極中にイッテルビウムおよびイッテルビウム化合物を添加することにより、ニッケル正極の高温における利用率を高め、水素吸蔵合金負極の合金腐食をおさえ、サイクル寿命を高めたニッケル水素化物蓄電池を完成するという極めて優れた効果が得られる。

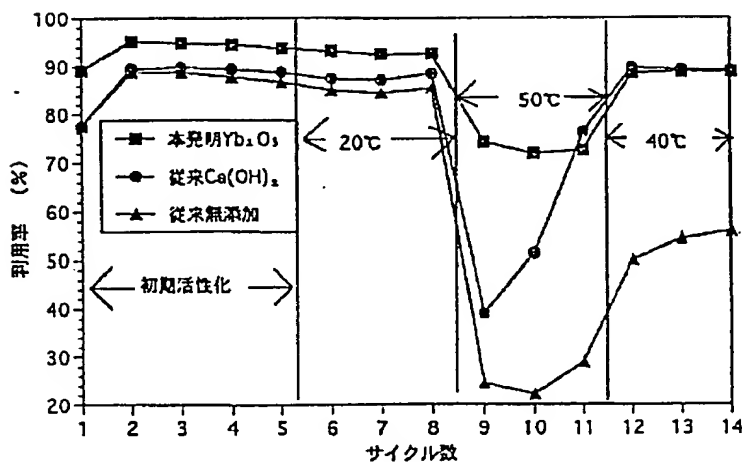
【図面の簡単な説明】

【図1】サイクル数と放電利用率の関係を示した図である。

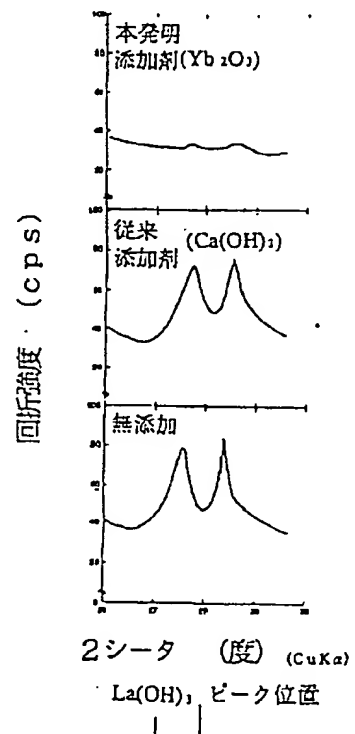
【図2】負極から取り出した水素吸蔵合金のX線回折を示した図である。

【図3】 $Yb_2O_3$ 添加量と放電利用率の関係を示した図である。

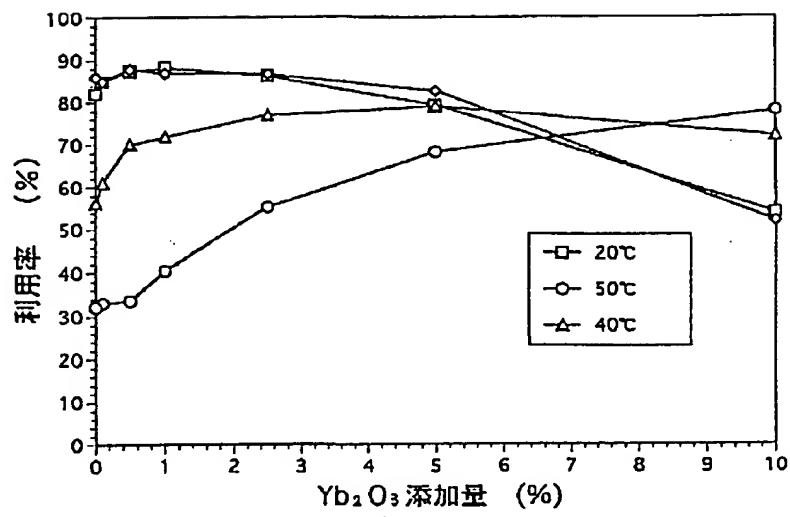
【図1】



【図2】



【図3】



フロントページの続き

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CLAIMS

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[Claim(s)]

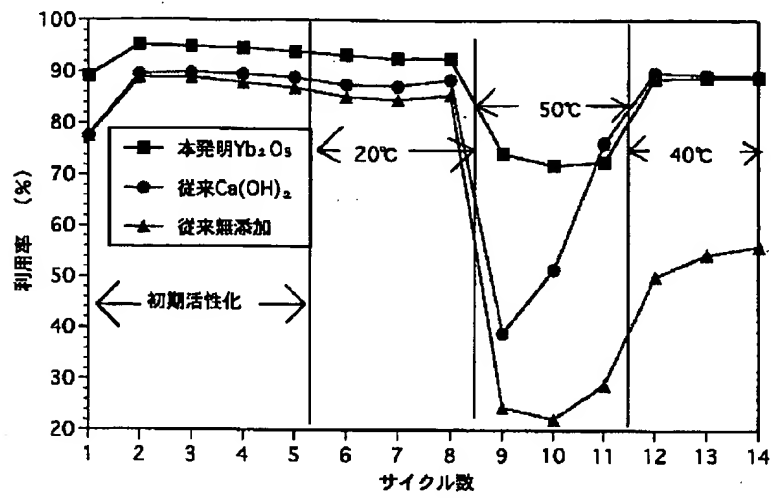
[Claim 1] The alkaline battery characterized by equipping the active material which makes a nickel hydroxide a principal component with the positive electrode which comes to add an ytterbium or a ytterbium compound.

[Claim 2] The active material to which an ytterbium or a ytterbium compound makes a nickel hydroxide a principal component in the aforementioned alkaline battery, and the alkaline battery according to claim 1 in which it exists by the free state.

[Claim 3] The alkaline battery according to claim 1 to which the ytterbium or the ytterbium compound exists all over the above-mentioned positive electrode in the state of an oxide or a hydroxide in the aforementioned alkaline battery.

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Drawing selection drawing 1

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## DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to the nickel hydride battery which used the nickel hydroxide and the hydrogen storing metal alloy.

[0002]

[Description of the Prior Art] It rides on the tendency of the environmental protection of these days, and the nickel hydride battery of low-pollution nature is used for a portable device etc. as a power supply replaced with the Ni-Cd battery which uses conventional cadmium for a negative electrode, and research and development are done briskly.

[0003] By the way, in the conventional Ni-Cd battery, in order to maintain the hot utilization factor of a nickel positive electrode, addition of cadmium was indispensable. In the nickel hydride battery characterized [ greatest ] by low-pollution nature, there was a problem that the cadmium which is the environmental destruction matter could not be used. As a means to solve this, the method of adding various additives, such as a lime compound, is reported so that a JP,5-290879, A official report etc. may see. However, there was a problem which is described below in a nickel hydride battery, and its additive was conventionally [ these ] inadequate for the cell performance improvement. On the other hand, in the strong base, the rare earth which is an alloy constituent began to melt, and the hydrogen storing metal alloy had the problem that a life became short in order to cause the corrosion phenomenon of depositing as an insulating hydroxide.

[0004]

[Problem(s) to be Solved by the Invention] this invention is made in view of the above-mentioned trouble, raises the hot utilization factor of a nickel positive electrode, presses down the alloy corrosion of a hydrogen storing metal alloy negative electrode, and completes the nickel hydride battery which raised the cycle life.

[0005]

[Means for Solving the Problem] By this invention, the above-mentioned trouble was solved by adding an ytterbium or a ytterbium compound to the nickel hydroxide positive electrode in a nickel hydride battery.

[0006] In a strong base, an ytterbium and a ytterbium compound melt slightly and deposit as a stable hydroxide. An ytterbium hydroxide has the effect of pulling up an oxygen-evolution overvoltage, and it raises the hot utilization factor of a nickel positive electrode in order to prevent decomposition of the electrolytic solution. Moreover, the ytterbium and ytterbium compound which were dissolved lengthen the life of a negative electrode, in order that a coat may be formed and this may prevent the corrosion of an alloy content, in case it deposits as a stable hydroxide on a hydrogen storing metal alloy negative-electrode front face.

[0007]

[Embodiments of the Invention] Based on an example, this invention is explained below.

(Example 1) for example, the nickel hydroxide of marketing which does not contain cadmium is



prepared and nickel hydroxide powder is received it becomes about Metal Co and becomes 4wt(s)% by weight % about CoO 6wt(s)% by weight % as an electric conduction agent -- as -- respectively -- adding -- for example, Yb 2O<sub>3</sub> weight % -- 2.5 % -- it fully mixed Water and the thickener were added to this and it was made the shape of a paste, for example, it pressed in the nickel fiber substrate after restoration and dryness, and accomplished with this invention nickel positive electrode, the usual hydrogen storing metal alloy electrode was made into the partner pole, and this invention nickel hydride battery was created using the alkali electrolytic solution.

[0008] On the other hand, it is calcium (OH)<sub>2</sub> as an additive conventionally to the nickel hydroxide powder of the same composition as the above because of comparison. The conventional positive electrode which does not use the added thing and an additive was created, the usual hydrogen storing metal alloy electrode was similarly made into the partner pole, and the nickel hydride battery for comparison was created using the alkali electrolytic solution. This cell for comparison is Yb 2O<sub>3</sub>. It is the completely same object as this invention nickel hydride battery except not containing all over a positive electrode.

[0009] Thus, charge and discharge were performed using this invention nickel hydride battery and the nickel hydride battery for comparison which were created. the result -- drawing 1 -- moreover, the oxygen-evolution overvoltage of these cells -- Table 1 -- it is shown, respectively

[0010]

[Table 1]

電池種類	酸素過電圧
本発明 (Yb <sub>2</sub> O <sub>3</sub> )	6.0 mV
従来例 (Ca(OH) <sub>2</sub> )	5.3 mV
従来例 無添加	5.1 mV

[0011] the inside of drawing 1 -- an electric discharge utilization factor -- a positive electrode -- a mixture -- inner nickel (OH)<sub>2</sub> what broke the actual service capacity when setting geometric capacity to 290mAh(s) per g by geometric capacity -- 100 It applies. Drawing 1 shows that this invention nickel hydride battery is maintaining sufficient capacity also in an elevated temperature as the Ming kana. Moreover, a passage clear from Table 1, compared with the conventional example, it is high, decomposition of the electrolytic solution is suppressed by this, and the oxygen overvoltage of this invention can prevent the capacity fall of a cell.

[0012] Furthermore, the cell after performing a cycle examination is disassembled, a hydrogen storing metal alloy is taken out from a negative electrode, and the result which performed the X diffraction is shown in drawing 2. Yb 2O<sub>3</sub> which is this invention so that more clearly than drawing 2 What was added has the small peak of the rare earth hydroxide near 29.2 theta, and it turns out that the alloy corrosion is stopped.

[0013] (Example 2) For example, nickel hydroxide powder is received like an example 1. It adds, respectively so that may become about Metal Co and it may become 4wt(s)% by weight % about CoO 6wt(s)% by weight % as an electric conduction agent, and it is Yb 2O<sub>3</sub> of various amounts. In addition, water and the thickener were added further, and it was made the shape of a paste, for example, it pressed in the nickel fiber substrate after restoration and dryness, and the nickel hydroxide positive electrode was created. Yb 2O<sub>3</sub> An addition is collectively shown in Table 2.

[0014]

[Table 2]

電池番号	Yb <sub>2</sub> O <sub>3</sub> 添加量%
1	0.1
2	0.5
3	1.0
4	2.5
5	5.0
6	10.0
7	0

[0015] The usual hydrogen storing metal alloy electrode was made into the partner pole in this nickel hydroxide positive electrode, and the nickel hydride battery was produced using the alkali electrolytic solution. Charge and discharge were performed using this cell. The result is shown in drawing 3. It is as [ from drawing 3 ] the Ming kana Yb 2O<sub>3</sub>. By adding shows that thermophylic ability is improved. since [ however, ] the utilization factor in ordinary temperature becomes bad and the effect in an elevated temperature becomes weak by addition below 0.5 % in 5% or more of addition -- weight % -- 0.5 from - - addition of 5.0 % is desirable

[0016]

[Effect of the Invention] As mentioned above, by the nickel hydride battery of this invention, by adding an ytterbium and a ytterbium compound all over a nickel hydroxide positive electrode, the hot utilization factor of a nickel positive electrode is raised, the alloy corrosion of a hydrogen storing metal alloy negative electrode is pressed down, and the extremely excellent effect of completing the nickel hydride battery which raised the cycle life is acquired.

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JAPANESE

[JP,09-092279,A]

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CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE  
INVENTION TECHNICAL PROBLEM MEANS DESCRIPTION OF DRAWINGS DRAWINGS

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[Translation done.]

JAPANESE

[JP,09-092279,A]

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[Translation done.]

JAPANESE

[JP,09-092279,A]

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JAPANESE

[JP,09-092279,A]

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## MEANS

[Means for Solving the Problem] By this invention, the above-mentioned trouble was solved by adding an ytterbium or a ytterbium compound to the nickel hydroxide positive electrode in a nickel hydride battery.

[0006] In a strong base, an ytterbium and a ytterbium compound melt slightly and deposit as a stable hydroxide. An ytterbium hydroxide has the effect of pulling up an oxygen-evolution overvoltage, and it raises the hot utilization factor of a nickel positive electrode in order to prevent decomposition of the electrolytic solution. Moreover, the ytterbium and ytterbium compound which were dissolved lengthen the life of a negative electrode, in order that a coat may be formed and this may prevent the corrosion of an alloy content, in case it deposits as a stable hydroxide on a hydrogen storing metal alloy negative-electrode front face.

[0007]

[Embodiments of the Invention] Based on an example, this invention is explained below.

(Example 1) for example, the nickel hydroxide of marketing which does not contain cadmium is prepared and nickel hydroxide powder is received it becomes about Metal Co and becomes 4wt(s)% by weight % about CoO 6wt(s)% by weight % as an electric conduction agent -- as -- respectively -- adding -- for example, Yb 2O<sub>3</sub> weight % -- 2.5 % -- it fully mixed Water and the thickener were added to this and it was made the shape of a paste, for example, it pressed in the nickel fiber substrate after restoration and dryness, and accomplished with this invention nickel positive electrode, the usual hydrogen storing metal alloy electrode was made into the partner pole, and this invention nickel hydride battery was created using the alkali electrolytic solution.

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[0009] Thus, charge and discharge were performed using this invention nickel hydride battery and the nickel hydride battery for comparison which were created. the result -- drawing 1 -- moreover, the oxygen-evolution overvoltage of these cells -- Table 1 -- it is shown, respectively

[0010]

[Table 1]

電池種類	酸素過電圧
本発明 ( $\text{Yb}_2\text{O}_3$ )	60mV
従来例 ( $\text{Ca}(\text{OH})_2$ )	53mV
従来例 無添加	51mV

[0011] the inside of drawing 1 -- an electric discharge utilization factor -- a positive electrode -- a mixture -- inner nickel (OH)<sub>2</sub> what broke the actual service capacity when setting geometric capacity to 290mAh(s) per g by geometric capacity -- 100 It applies. Drawing 1 shows that this invention nickel hydride battery is maintaining sufficient capacity also in an elevated temperature as the Ming kana. Moreover, a passage clear from Table 1, compared with the conventional example, it is high, decomposition of the electrolytic solution is suppressed by this, and the oxygen overvoltage of this invention can prevent the capacity fall of a cell.

[0012] Furthermore, the cell after performing a cycle examination is disassembled, a hydrogen storing metal alloy is taken out from a negative electrode, and the result which performed the X diffraction is shown in drawing 2. Yb<sub>2</sub>O<sub>3</sub> which is this invention so that more clearly than drawing 2 What was added has the small peak of the rare earth hydroxide near 29 2 theta, and it turns out that the alloy corrosion is stopped.

[0013] (Example 2) For example, nickel hydroxide powder is received like an example 1. It adds, respectively so that may become about Metal Co and it may become 4wt(s)% by weight % about CoO 6wt(s)% by weight % as an electric conduction agent, and it is Yb<sub>2</sub>O<sub>3</sub> of various amounts. In addition, water and the thickener were added further, and it was made the shape of a paste, for example, it pressed in the nickel fiber substrate after restoration and dryness, and the nickel hydroxide positive electrode was created. Yb<sub>2</sub>O<sub>3</sub> An addition is collectively shown in Table 2.

[0014]

[Table 2]

電池番号	Yb <sub>2</sub> O <sub>3</sub> 添加量%
1	0.1
2	0.5
3	1.0
4	2.5
5	5.0
6	10.0
7	0

[0015] The usual hydrogen storing metal alloy electrode was made into the partner pole in this nickel hydroxide positive electrode, and the nickel hydride battery was produced using the alkali electrolytic solution. Charge and discharge were performed using this cell. The result is shown in drawing 3. It is as [ from drawing 3 ] the Ming kana Yb<sub>2</sub>O<sub>3</sub>. By adding shows that thermophylic ability is improved. since [ however, ] the utilization factor in ordinary temperature becomes bad and the effect in an elevated temperature becomes weak by addition below 0.5 % in 5% or more of addition -- weight % -- 0.5 from - addition of 5.0 % is desirable



[Translation done.]

JAPANESE

[JP,09-092279,A]

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CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE  
INVENTION TECHNICAL PROBLEM MEANS DESCRIPTION OF DRAWINGS DRAWINGS

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[Translation done.]

**JAPANESE** [JP,09-092279,A]

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[Translation done.]